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NEUTRON DIFFRACTION STUDY OF α - $\text{Pb}(\text{N}_3)_2$

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INTRODUCTION:—The azide ion is one of the simple examples of a metastable or explosive molecule ion. Lead azide among the inorganic azide salts is widely used as a military and commercial primary explosive. For this reason extensive studies of the chemistry and decomposition kinetics of lead azide have been undertaken in the last fifteen years. Recently, attempts have been made to explain these results, especially the explosive behavior, in terms of solid state physical and chemical processes. A need for information of the detailed crystal structure of lead azide has prompted this investigation. The detailed structure of the azide ions in lead azide was of principal interest. Theories of the stability of the azides usually use degree of covalent bonding as the principal variable for determining the sensitivity and other explosive properties. The symmetry of the azide ion is thought to reflect the degree of covalent bonding in the solid. Therefore, detailed structural work will play a crucial role in formulating a more detailed theory.

There are four known polymorphic forms of lead azide designated as the α -, β -, γ - and δ -forms. The first complete investigation of the α - β polymorphism in lead azide was performed by F. D. Mile (1). Later, Pfefferkorn (2) and Azaroff (3) attempted to determine the space group of these two forms by x-ray investigation. In the alpha-lead azide study, Azaroff deduced two possible groups, $\text{Pc}2_1\text{n}$ and Pcmm , from the Pb atom configuration. He concluded that $\text{Pc}2_1\text{n}$ is the probable space group because his infrared data favored an asymmetric structure for the azide group and because packing considerations of the azide group in the Pcmm space group require at least one symmetric azide group. He determined the approximate position of the Pb atoms but could not give N atom positions because the Pb atom dominated the intensity of the x-ray scattering. Glen (4) has recently analyzed the two dimensional neutron diffraction data of Danner and Kay. He obtained approximate positions for the N atoms in the non-centrosymmetric space group $\text{Pc}2_1\text{n}$, but failed to investigate the details of atomic bonding because the X-coordinates

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were not directly determined and also because the standard deviation of the remaining parameters were rather large. In the present study the centrosymmetric space group $Pcmm$ and Azaroff's cell parameters, $a=11.31\text{\AA}$, $b=16.25\text{\AA}$, $c=6.63\text{\AA}$, were used to fit this neutron diffraction measurement.

EXPERIMENTAL: A small crystal of lead azide in the form of a flat rhombic prism, 3 mm thick, 5 mm wide, and 8 mm long was mounted on the 3 dimensional goniometer cradle. The crystal was aligned so that the crystallographic c-axis was parallel to the rotation axis of the goniometer. The diffraction intensities were measured by constant speed scanning with a GE X-ray diffractometer modified for neutron diffraction. Due to the difficulty of making the correction for the crystal geometry, the goniometer Chi-angles were limited to less than 30 degrees, which restricted the l -value of the (hkl) planes to a maximum of 4. Using a 1.055\AA wavelength neutron beam, a total of 888 reflection planes were investigated of which 285 planes were too weak to detect, and about 170 more were very weak. The $(0kl)$ reflection data were compared with those collected previously at this laboratory using a different crystal. Of the 71 earlier $(0kl)$ reflections, 16 are common and show excellent agreement with the data of the present investigation. The $(0kl)$ data of the 55 non-overlapping planes were added by assigning them an independent scale factor.

The estimated μ_R (characteristic absorption of this crystal) ranged from about 0.1 to 0.15. The absorption corrections were neglected because the effect is small. No secondary extinction effects were observed during the refinement procedure.

REFINEMENT: The least squares refinement was carried out with the ORFLS program (5) modified at Argonne National Laboratory for the CDC 3500 computer. The zero-intensity reflections were included for the refinement by assigning them an arbitrary intensity of 3.0 with an independent scale factor. As an initial trial, Glen's structure (4) was refined using the $Pc2_1n$ space group. With this non-centrosymmetric space group, the R factor of the least squares refinement with isotropic temperature factors became 0.138 for all data, 0.09 excluding zero intensity reflections, and 0.091 excluding zero - and very weak intensity reflections. The atomic arrangement of this non-centrosymmetric space group was almost the same as the result obtained by Glen. However, as the refinement progressed, the atomic positions oscillated randomly without reducing the R factor. In particular, the symmetry of the azide groups varied in such a manner that they were related by a mirror plane at $y=1/4$. Refinement including anisotropic thermal vibrations was attempted. This failed because the anisotropic temperature factor of some nitrogen atoms became negative especially for the azide ions coupled by the mirror plane.

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In the course of the refinement with the non-centrosymmetric space group, one of the azides (designated azide I in the later section) was symmetric in form throughout the refinement. The overall atomic configuration showed centrosymmetry with a mirror plane at $y=1/4$, which lead to the space group $Pcmn$. The atoms were then re-assigned to the unit cell of this new space group, $Pcmn$, by moving the atomic coordinates less than 2 standard deviations. In this space group 8 Pb and 56 N atoms were assigned to general positions (site d), and 4 Pb and 16 N atoms were assigned to special positions (site c), which gives a total of 13 atoms in the asymmetric unit. With this centrosymmetric space group, the refinement converged rapidly and the atomic positions were quickly stabilized. The R factor of the refinement with isotropic temperature was about the same but the standard deviations were reduced to one third of the values found by using the non-centrosymmetric space group. With anisotropic temperature factors, the R factor was further reduced to $R=0.108$, $wR=0.102$ for all reflection data including zero intensity. The final parameters of the least squares refinement with anisotropic temperature factors for all reflection data including zero intensity are given in Table 1. When the zero intensity and very weak intensity reflections were excluded, the R factor was reduced to 0.07 but the standard deviations were somewhat increased. All observations including zero intensity reflections were given unit weight in the refinement. As fractions of the standard deviations, the maximum shift was 0.003 in the last cycle.

AZIDE STRUCTURE: There are 4 different types of azide groups in α -lead azide as shown in Figure 1. The azide (I) is linear and symmetric with $N-N = 1.164\text{\AA}$. This azide group has a mirror plane perpendicular to the azide axis through the center N atom. Consequently, the whole system including the two nearest neighboring Pb atoms at both ends shows mirror symmetry. There are 4 azide (I) ions in a unit cell and they are all parallel to the b-axis. Each of the 2 neighboring azides is bonded to a common Pb atom forming a continuous chain of Pb atoms alternating with terminal azide nitrogens parallel to the c-axis.

The azide (II) is essentially linear (177° in angle N-N-N) but slightly asymmetric with $N'-N'' = 1.19\text{\AA}$ and $N''-N''' = 1.17\text{\AA}$. Unlike the symmetric environment of the azide (I), the bond distances to the 2 Pb atoms at each end is quite different, 2.6\AA at one end and 2.9\AA at the other end. They also form a bond chain extending along the c-axis, but the direction of the two Pb-N bonds at each end are twisted with respect to each other by an 80° rotation along the azide axis. The structure of azide (III) is also linear and shows clear asymmetry with $N'-N'' = 1.19\text{\AA}$ and $N''-N''' = 1.16\text{\AA}$. The azide (III) is also bonded to 2 Pb atoms at each end with the bond direction twisted by 80° in the same way as azide (II). The bond chain forms a 2 dimensional pattern, covering the (100) plane. There are 2 azide (II) and 8 azide (III) groups in a unit cell.

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Azide (IV) is linear and strongly asymmetric with $N'-N'' = 1.21\text{\AA}$ and $N''-N''' = 1.15\text{\AA}$. This azide is located in the mirror plane as are its Pb neighbors. The terminal N atom of the longer N-N bond is also weakly bonded to 2 more Pb atoms one on either side of the mirror plane. Azide (IV) groups also form a chain parallel to the c-axis with the Pb atom bonded to alternate terminal nitrogens of each azide group. There are 4 azide (IV) in a unit cell.

The angle between the Pb-N bond and the azide axes varies over a wide range, mostly between 105° and 128° except 150° in azide (II) and 180° in azide (IV). Each azide is confined in its own domain formed by the neighboring Pb atoms and stacked along the c-axis as shown in Figure 2. The domain size of the azides (I), (II), (III) and (IV) is 0.0817, 0.0814, 0.0878 and 0.0835 respectively as a fraction of area formed by a- and b-axis. Since the corresponding azide lengths are 2.328\AA , 2.343\AA , 2.356\AA and 2.306\AA , the relative packing density (the ratio of azide length to domain area) are 28.5, 28.8, 26.8 and 28.1 respectively. As a result, the terminal atoms of azides (I) and (II), and the center atom of azide (IV) are within the sum of the Van der Waal's radii as discussed in a later section. Perhaps the slight bending of the azide (II) and azide (IV) may be caused by this packing strain.

ATOMIC ARRANGEMENT: There are 12 $\text{Pb}(\text{N}_3)_2$ molecules in a unit cell. The 4 types of azide groups may be reclassified into 2 categories, namely symmetric (azide I and II) and asymmetric (azide III and IV), in accordance with the degree of symmetry. Then it is observed that the symmetric and asymmetric azides are arranged in different layers oriented perpendicularly to the a-axis and separated by a layer of Pb atoms. Each Pb atom is bonded by 8 azides with bond distances ranging from 2.57\AA to 2.90\AA , and further surrounded by 4 Pb atoms at distances of 4.20, 4.36, 4.38 and 4.53\AA . The details of interatomic distances are given in Table 3. The closest approach between neighboring azides is 2.95\AA (II-IV) and is 2.97\AA between I and II. This is equivalent to the sum of the Van der Waal's radii of N atoms given by Pauling (10).

The 8 Pb-N bonds from each Pb atom in α -lead azide form a distorted tetragonal antiprismatic arrangement. In other words the bond directions extend from the body centered Pb atom toward the 8 corners of 2 opposing distorted tetragons. The tetragonal bases of the antiprism differ in distortion, one is rectangular and the other is rhombic or a parallelogram [in $\text{Pb}(2)$], as shown in Figure 3. In the $\text{Pb}(1)$ atom the rectangular prismatic bonds are much longer than the rhombic prismatic bonds, and in the $\text{Pb}(2)$ atom it is also generally longer than those of the parallelogram bonds. It is likely that the rhombic prismatic bonds are quite stable but the tetragonal distortion of the tetragonal prismatic bonds may tend to be unstable (or weaker). The rectangular prismatic bonds of $\text{Pb}(1)$ and the parallelogramic bonds of $\text{Pb}(2)$ are bonded to the azides in a symmetric

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layer. The rectangular bonds of Pb(2) and the rhombic bonds of Pb(1) are bonded to those of the asymmetric layer.

SUMMARY: The 3 dimensional neutron diffraction study has shown that α -lead azide crystallizes in the orthorhombic Pcmn space group. There are 4 types of azide groups and these differ in their degree of symmetry and environment. Each type of azide is stacked compactly within a domain bounded by neighboring Pb atoms along the c-axis direction.

The symmetric azide (I) and the almost symmetric azide (II) form a layer and the asymmetric azide (III) and (IV) form another layer in this structure. Lead atoms are located between these two layers and each is bonded to 8 azides in a distorted tetragonal antiprismatic arrangement, 4 bonds directed toward the "symmetric" azide layer and the other 4 toward the "asymmetric" layer.

The N-N distances in azide (I) and (II) in the symmetric azide layer agree with those found in the ionic azides. The N-N distances of the monovalent azide ion are reported as 1.17Å for NaN_3 (6), NH_4N_3 (7) and CuN_3 (8), and 1.16Å for KN_3 (6), and AgN_3 (9), and 1.15Å for NaN_3 and KN_3 (7). It is believed that the azides in the symmetric layer are mainly ionic in character. The N-N distances of the asymmetric azides (III) and (IV) are similar to those found in covalent azides. They are 1.24Å and 1.13Å for HN_3 (11) and 1.26Å and 1.10Å in CH_3N_3 (12). From these comparisons and consideration of bond symmetry from Figure 3, it is deduced that the 4 lead azide bonds directed toward the asymmetric azide layer have more covalent character, forming 4 covalent bonds laying to one side as the case of tetragonal PbO (13) and orthorhombic PbO (14).

In summary, the detailed crystal structure of the primary explosive α -lead azide has been determined using neutron diffraction techniques. Besides giving clarification and confirmation of previous work definite asymmetry has been discovered in the four types of azide ions in this structure. The possible implication of this finding to the degree of covalent bonding and explosive behavior has been discussed.

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Table 1

Final Least Squares Parameters with Standard Deviations

Atom	X	Y	Z	δ_{11} ($\times 10^5$)	δ_{22} ($\times 10^5$)	δ_{33} ($\times 10^5$)	δ_{12} ($\times 10^5$)	δ_{13} ($\times 10^5$)	δ_{23} ($\times 10^5$)
Pb(1)	-0.1359(4)	0.2500(0)	0.0595(11)	323(27)	170(14)	253(182)	0(0)	22(55)	0(0)
Pb(2)	0.1236(3)	0.0884(2)	0.3418(8)	288(19)	137(9)	146(203)	-6(10)	-75(45)	-35(27)
N(1)	0.2802(3)	0.1784(2)	0.1528(10)	540(27)	137(9)	1585(166)	-2(13)	410(65)	33(31)
N(2)	0.2798(4)	0.2500(0)	0.1529(14)	395(32)	117(12)	713(351)	0(0)	221(74)	0(0)
N(3)	-0.2641(3)	-0.0015(2)	0.4338(9)	427(23)	138(9)	948(98)	-24(12)	-134(54)	-2(29)
N(4)	-0.2370(3)	0.0664(2)	0.3933(7)	306(20)	135(9)	385(118)	-45(11)	-173(45)	59(26)
N(5)	-0.2143(4)	0.1340(2)	0.3485(9)	651(30)	184(11)	940(141)	-116(15)	-120(71)	86(36)
N(6)	0.0059(3)	0.1286(2)	-0.0055(9)	432(23)	208(12)	925(130)	88(14)	-143(57)	-242(36)
N(7)	0.0014(3)	0.0904(2)	-0.1588(9)	268(20)	153(10)	683(254)	29(11)	-13(45)	4(34)
N(8)	-0.0032(4)	0.0536(2)	-0.3085(8)	546(27)	178(11)	603(110)	-72(14)	254(60)	-219(32)
N(9)	0.0144(4)	0.2500(0)	0.3587(11)	281(29)	231(16)	334(182)	0(0)	-170(80)	0(0)
N(10)	-0.0396(4)	0.2500(0)	0.5168(11)	357(30)	107(12)	472(174)	0(0)	-21(87)	0(0)
N(11)	-0.0924(3)	0.2500(0)	0.6645(17)	526(44)	263(20)	870(349)	0(0)	-203(117)	0(0)

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Table 2

Dimensions of Azide Group
(with standard deviations)

Azide	N'-N''(Å)	N''-N'''(Å)	N'-N''-N'''(°)
I	1.164(3)	1.164(3)	179.5(6)
II	1.177(5)	1.166(5)	177.3(5)
III	1.193(8)	1.160(8)	179.7(5)
IV	1.213(10)	1.147(13)	178.8(8)

Table 3

Bond Distances and Angles Between Pb Atoms and Azides
(with standard deviations)

Atoms	Azides	No.	Distances (Å)	Angles (°)
Pb(1)	N(5,4,3)	2	2.896(7)	110.8(2)
Pb(1)	N(5,4,3)	2	2.831(7)	149.9(3)
Pb(1)	N(6,7,8)	2	2.578(5)	120.8(3)
Pb(1)	N(9,10,11)	1	2.612(8)	106.6(3)
Pb(1)	N(11,10,9)	1	2.665(14)	159.8(4)
Pb(2)	N(1,2,1)	1	2.617(6)	124.0(1)
Pb(2)	N(1,2,1)	1	2.753(7)	122.1(1)
Pb(2)	N(3,4,5)	1	2.635(6)	116.9(3)
Pb(2)	N(3,4,5)	1	2.595(6)	120.2(2)
Pb(2)	N(6,7,8)	1	2.738(7)	128.0(2)
Pb(2)	N(8,7,6)	1	2.689(4)	122.5(3)
Pb(2)	N(8,7,6)	1	2.785(7)	125.7(2)
Pb(2)	N(9,10,11)	1	2.904(4)	104.5(2)

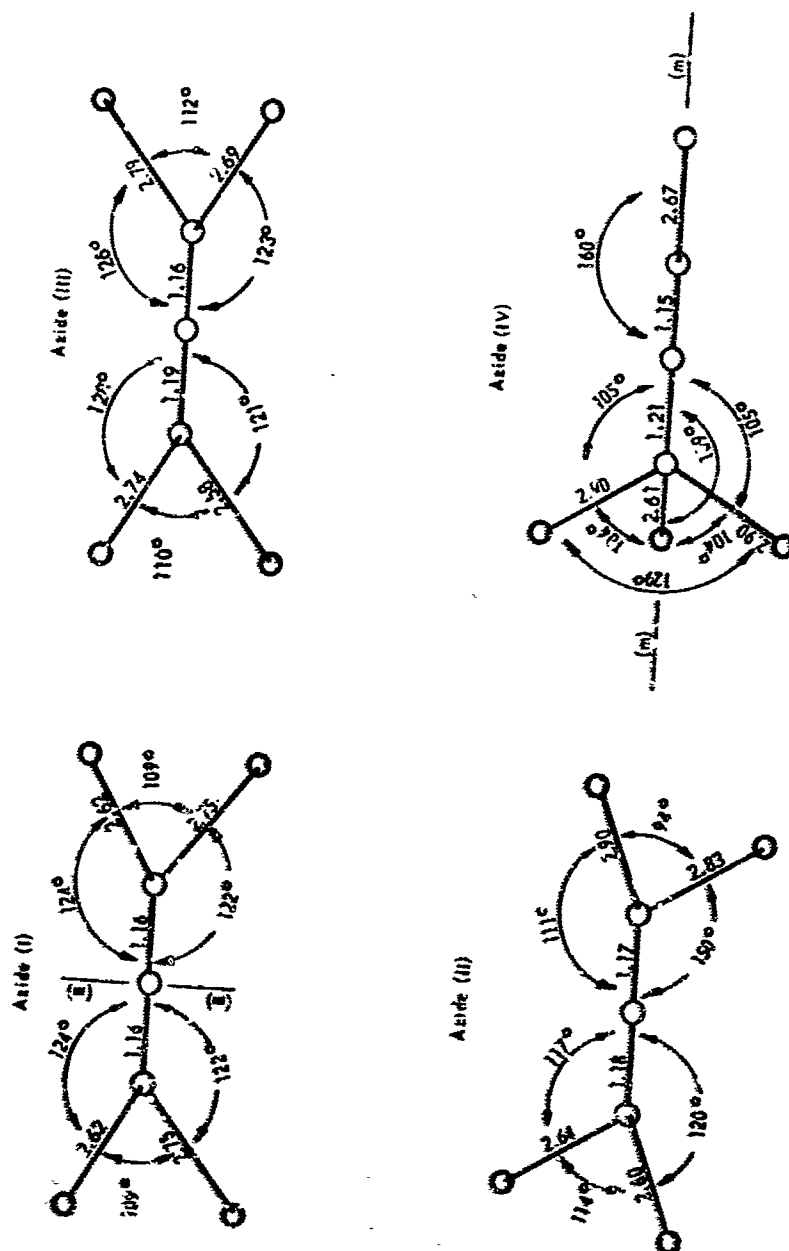


FIGURE 1. SCHEMATIC ILLUSTRATION OF THE STRUCTURE OF THE AZIDE GROUPS AND POSITIONS OF THE NEIGHBORING Pb ATOMS.

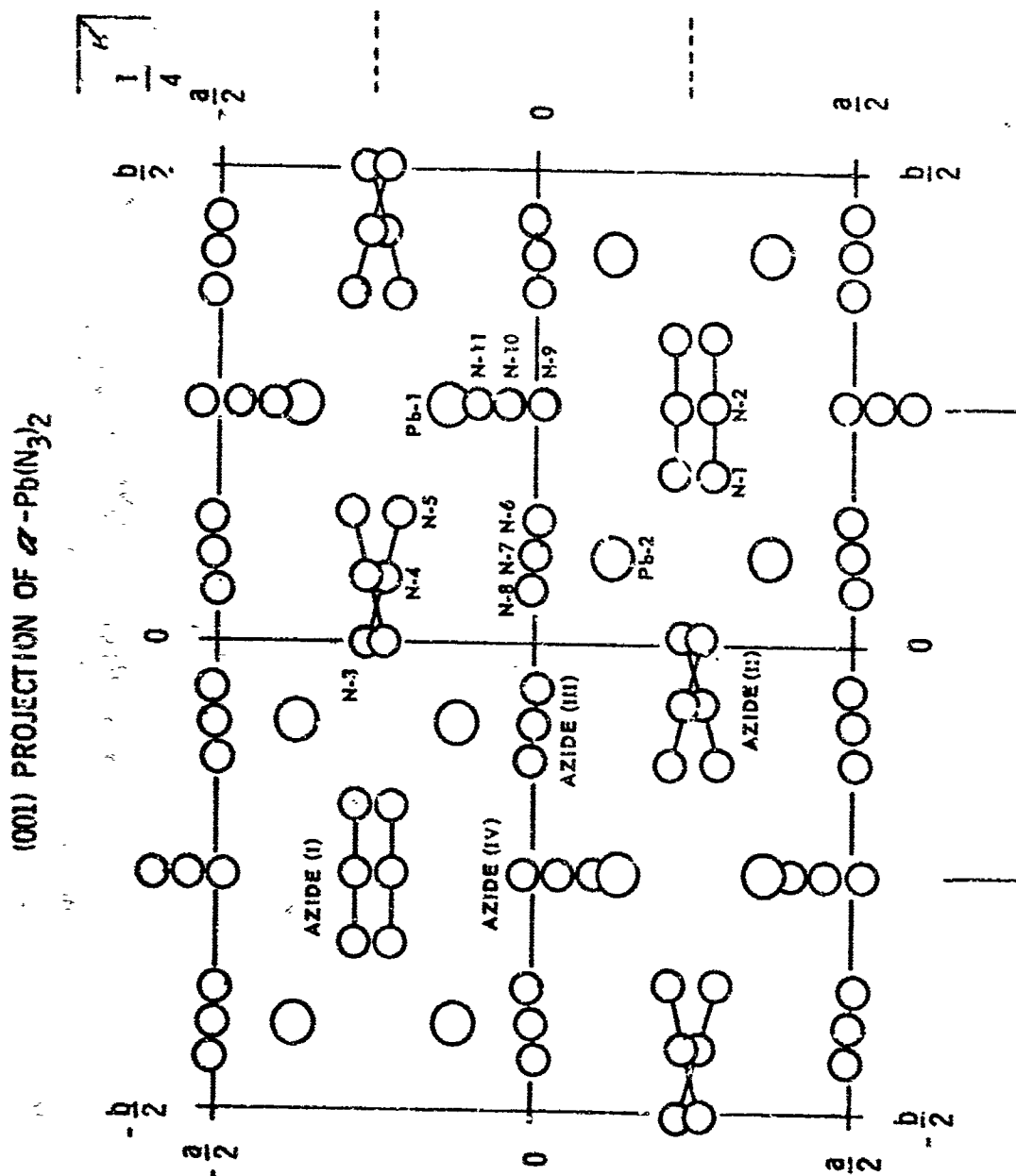


FIGURE 2. ATOMIC ARRANGEMENT IN A UNIT CELL, AS VIEWED ALONG THE C-AXIS. THE LEAD ATOMS ARE REPRESENTED BY THE LARGE CIRCLES AND THE NITROGENS BY SMALL CIRCLES.

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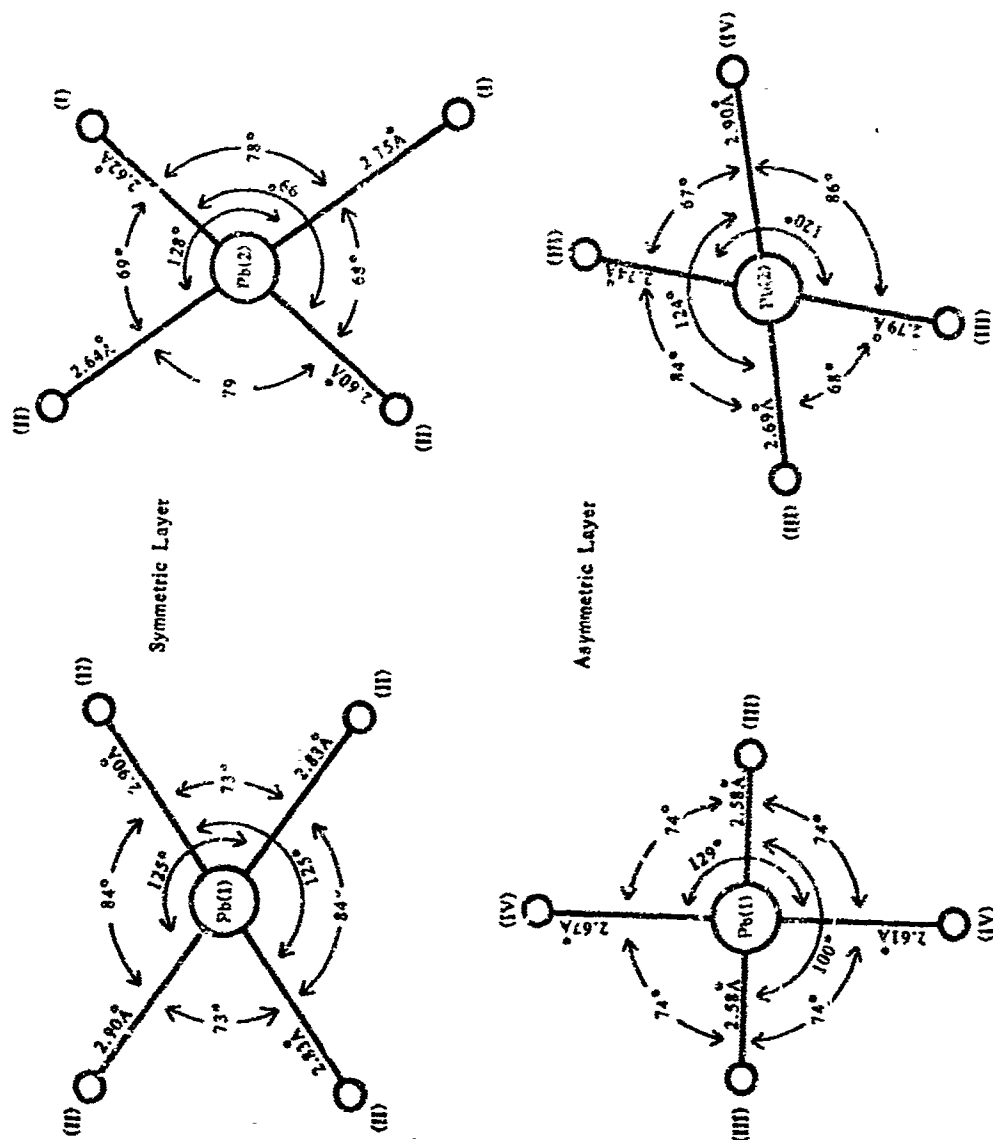


FIGURE 3. DIAGRAM TO ILLUSTRATE THE BOND ARRANGEMENTS OF Pb(1) AND Pb(2) ATOMS IN α -Pb(N₃)₂. IN THE FIGURE, (I), (II), ETC. REFER TO AZIDE (I), AZIDE (II), ETC.